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(54) Title of the Invention:

SILICON CARBIDE SINTERED PRODUCT HAVING A PROTECTIVE  
FILM WITH EXCELLENT CORROSION RESISTANCE AND  
A METHOD FOR ITS PRODUCTION

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## SPECIFICATION

1. Title of the Invention: A silicon carbide sintered product having a protective film with excellent corrosion resistance and a method for its production

2. Scope of the Patent Claims:

(1) Silicon carbide sintered product having a dense and corrosion-resistant protective film made of a eutectic oxide consisting of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  as its main components.

(2) Silicon carbide sintered product as described in Claim 1, characterized in that the aforementioned  $\text{SiO}_2$  is mainly the  $\text{SiO}_2$  formed by oxidation of the silicon carbide sintered product.

(3) Silicon carbide sintered product as described Claim 1 or Claim 2, characterized in that the thickness of the aforementioned film is in the range of 0.5-25  $\mu\text{m}$ .

(4) Silicon carbide sintered product as described in any one of Claims 1-3 of the Scope of the Patent Claims, characterized in that the  $\text{Al}_2\text{O}_3/\text{SiO}_2$  molar ratio of the  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  contained in the aforementioned protective film is in the range of 0.024-1.8.

(5) Silicon carbide sintered product as described in any one of Claims 1-4 of the Scope of the Patent Claims that can be used in a skid button or skid rail.

(6) Method for the production of a silicon carbide sintered product having a dense and corrosion-resistant protective film, which is characterized in that the surface of the silicon carbide sintered product is coated with an aluminum-containing substance and then heated and oxidized in an oxidative atmosphere to form a protective film layer made of a eutectic oxide with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  as its main components.

(7) Method of production as described in Claim 6 of the Scope of the Patent Claims, characterized in that the heating temperature in the aforementioned oxidative atmosphere is in the range of 750-1,650°C.

(8) Method of production as described in Claim 6 or Claim 7 of the Scope of the Patent Claims, characterized in that the film thickness of the aforementioned insulating film is in the range of 0.5-25  $\mu\text{m}$ .

(9) Method of production as described in any one of Claims 6-8 of the Scope of the Patent Claims, characterized in that the aforementioned aluminum-containing substance is at least a substance selected from among the group consisting of alumina sol, metallic aluminum, aluminum-containing alloys, aluminum oxide, aluminum hydroxide, aluminates, aluminum silicate, aluminum phosphate, and aluminum acetate.

(10) Method of production as described in any one of Claims 6-9 of the Scope of the Patent Claims, characterized in that the amount of the aforementioned aluminum-containing substance coating is in the range of 0.004-2.9  $\text{mg}/\text{cm}^2$  in terms of  $\text{Al}_2\text{O}_3$ .

### 3. Detailed Description of the Invention

The present invention pertains to a silicon carbide sintered product suitable for use as a high-temperature structural material and a method for its production. To be more specific, the present invention pertains to a silicon carbide sintered product having a very dense protective film with excellent corrosion resistance.

A heat treatment furnace such as a soaking pit, annealing furnace, etc., is generally used in the production of iron and steel. The steel materials to be heat-treated in this way are placed on a supporting platform such as a skid button or a skid rail in a

heat treatment furnace and heat-treated. The aforementioned supporting platform such as a skid button or skid rail is usually made of water-quenched steel. However, when the aforementioned supporting platform made of water-quenched steel is used as described above, an extreme heat gradient forms between that part of the to-be-heated steel material making contact with the supporting platform and other parts of the steel material. This extreme heat gradient not only can lower the heating efficiency but also can produce defects in the steel material, such as a skid marks, etc.

The fact that sintered silicon carbide is very suitable for use as a high-temperature structural material under harsh conditions, especially for the parts of gas turbines, heat exchangers, etc., because it shows excellent chemical and physical characteristics, especially its high-temperature strength and anti-spalling properties, and because it is one of the most oxidation-resistant substances among the various carbides, has attracted our attention. Accordingly, we investigated the possible use of a silicon carbide sintered product in the support platforms described above. However, a silicon carbide sintered product can be easily corroded upon contact with a metal having strong reactivity, such as steel, in a high-temperature region. Therefore, when a silicon carbide sintered product is used as a support platform for a to-be-heated material in the aforementioned heat treatment furnace, the Si or C elements making up the silicon carbide sintered product will be decomposed at the point of contact between the silicon carbide sintered product and the steel and diffuse into the steel, thus contaminating it. In addition, the silicon carbide sintered product will be corroded and consumed. Therefore, it is difficult to use a silicon carbide sintered product in applications in which the silicon carbide sintered product makes direct contact with a metal with strong reactivity, such as

steel, in a high-temperature region.

Previously, we studied electronic circuit boards with excellent characteristics suitable for use as an integrated circuit board or IC package and proposed "A silicon carbide base board having an insulating surface film with excellent adhesiveness and with a eutectic oxide of aluminum oxide and silicon dioxide as its main component" in Japanese Patent Application No. 56 [1981]-209,991. The silicon carbide base board of the aforementioned invention possesses a surface film for the purpose of providing an insulating property at normal temperatures.

We thought that a silicon carbide sintered product having properties similar to those of the silicon carbide base board of the aforementioned invention might be suitable for use as a support platform for a to-be-heat-treated material in a heat-treatment furnace that is destined to be used at an elevated temperature. This thought led us to develop the present invention. In other words, by allowing a film made of a eutectic oxide with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  as its main components to form on the surface of a silicon carbide sintered product, the silicon carbide sintered product can be used as a suitable support platform for a to-be-heat-treated material in a heat-treatment furnace, where said material is destined to be used in an elevated temperature environment.

The purpose of the present invention is to provide a silicon carbide sintered product capable of eliminating the aforementioned shortcomings. To be more specific, the purpose of the present invention is to provide a silicon carbide sintered product having a dense protective film with an excellent anti-corrosion property.

In accordance with the present invention, the aforementioned purpose can be achieved by a silicon carbide sintered product having a dense protective film with

excellent corrosion resistance made of a eutectic oxide with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  as its main components and by a method for its production.

The present invention will now be explained in detail.

In the present invention, the aforementioned protective film must be made of a eutectic oxide with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  as its main components. The aforementioned  $\text{SiO}_2$  is preferably mainly  $\text{SiO}_2$  formed as the result of oxidation of the silicon carbide sintered product. The aforementioned protective film made of a eutectic oxide with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  as its main components should be very dense, should have no defects such as pinholes, etc., and should have excellent corrosion resistance. The  $\text{SiO}_2$  formed by the oxidation of silicon carbide will readily form an oxide in a mutually eutectic state with  $\text{Al}_2\text{O}_3$  present on the surface of the silicon carbide sintered product even at a relatively low temperature. In addition, it can form a protective film that contains a transition layer incorporating the silicon carbide sintered product and having excellent adhesiveness with the silicon carbide sintered product.

In the present invention, the thickness of the aforementioned protective film is preferably in the range of 0.5-25  $\mu\text{m}$ , because if the thickness of the aforementioned protective film is less than 0.5  $\mu\text{m}$ , it will be difficult to obtain a stable protective effect on the silicon carbide sintered product, thus the product will be less reliable. In contrast, if the thickness is greater than 25  $\mu\text{m}$ , the effect of the difference in the thermal expansion coefficients of the protective film and the silicon carbide sintered product may become great enough to cause the formation of cracks, etc., thus lowering the reliability. Furthermore, in an extreme case, the protective film may peel off. The optimum range of the film thickness is 1.0-15  $\mu\text{m}$ .

In the present invention, the amounts of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  contained in the aforementioned protective film in terms of the  $\text{Al}_2\text{O}_3/\text{SiO}_2$  molar ratio is preferably in the range of 0.024-1.8. If the aforementioned  $\text{Al}_2\text{O}_3/\text{SiO}_2$  molar ratio is less than 0.024, the prevention effect on the cristobalite formation of the  $\text{SiO}_2$  that forms as the result of the oxidation of silicon carbide will not be sufficient and a uniform and dense film cannot be obtained. In contrast, if the molar ratio is greater than 1.8, the melting point of the eutectic oxide will become high and the formation of a uniform film will become difficult. In addition, the difference in the thermal expansion coefficients of the film and the silicon carbide sintered product will increase, which tends to make the film peel off easily. The best result can be obtained when the ratio is in the range of 0.05-1.0.

The silicon carbide sintered product of the present invention is very suitable as a high-temperature structural material for use in the temperature range above  $750^\circ\text{C}$  and is especially suitable for use in an oxidative environment in a temperature range of  $1,100-1,500^\circ\text{C}$ .

A method for the production of the silicon carbide sintered product of the present invention having a protective film with excellent corrosion resistance will now be described.

In the present invention, the surface of a silicon carbide sintered product is pre-coated with an aluminum-containing substance and then oxidized by heating in an oxidative environment to form a protective film made of a eutectic oxide with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  as its main components on said surface.

In the present invention, the aforementioned aluminum-containing substance will become  $\text{Al}_2\text{O}_3$  in the oxidative environment at the time of formation of the

aforementioned eutectic oxide. The amount of this substance being coated is in the range of 0.004-2.9 mg/cm<sup>2</sup> in terms of Al<sub>2</sub>O<sub>3</sub> so that the thickness of the protective film formed will be in the range of 0.5-25 μm and the Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> molar ratio of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> will be in the range of 0.024-1.8. At least one substance selected from a group of substances consisting of, for example, alumina sol, metallic aluminum, aluminum-containing alloys, aluminum oxide, aluminum hydroxide, aluminates, aluminum silicate, aluminum phosphate, and aluminum acetate is preferably used as the aforementioned aluminum-containing substance. The use of alumina sol works particularly well because it can provide very fine Al<sub>2</sub>O<sub>3</sub> with high reactivity at the time of formation of the aforementioned eutectic oxide.

In the present invention, the heating temperature of the aforementioned oxidative environment is preferably in the range of 750-1,650°C. When the aforementioned temperature is below 750°C, the rate of oxidation of the silicon carbide sintered product will be very slow and the process will not be practical. In contrast, when the temperature is above 1,650°C, the rate of oxidation of the silicon carbide sintered product will become exceptionally rapid, making it difficult to control the film thickness within the specified range. In addition, CO gas, etc., which form as a result of the oxidation of silicon carbide will create bubbles in the space between the film and the silicon carbide sintered product, which makes it difficult to obtain a uniform oxidized film with excellent adhesiveness.

In the present invention, in order to promote the eutectic process of the aforementioned eutectic oxide and to promote adhesiveness with the silicon carbide sintered product, the surface of the silicon carbide sintered product may be coated with at



least one substance selected from a group of substances consisting of alkali metal-containing substances and alkali earth metal-containing substances. The aforementioned alkali metal-containing substances and alkali earth metal-containing substances will become oxides of alkali metals or alkali earth metals in the oxidative environment at the time of formation of the protective film formed from the aforementioned eutectic oxide. The amount of the substance to be coated is preferably less than  $5 \text{ mg/cm}^2$  in terms of the oxide and if the melting point lowering of the eutectic oxide is taken into consideration, the smaller the amount coated the better. It is especially advantageous if the amount to be coated is less than  $2.5 \text{ mg/m}^2$ . The aforementioned alkali metals and alkali earth metals include, for example, Li, Na, K, Be, Mg, Ca, etc. These elements or their compounds may be used individually or in various combinations.

In the present invention, the aforementioned protective film may contain oxides of P, B, Ge, As, Sb, Bi, V, Zn, Cd, or Pb.

In the present invention, it is advantageous to allow the aforementioned oxidative environment to contain water vapor. This is because the water vapor contained in the aforementioned environment can promote the oxidation of silicon carbide and a protective film made of a eutectic oxide can be formed efficiently even at a relatively low temperature.

The present invention will now be explained with the use of actual examples.

#### Actual Example 1

The silicon carbide sintered product used was a sintered product with no pressurization containing 1.0 weight % of boron and 2.0 weight % of free carbon and

having a density of  $3.1 \text{ g/cm}^3$ . It was obtained by subjecting a plate-shaped silicon carbide sintered product measuring  $20 \times 20 \times 5 \text{ mm}$  to an initial polishing process and then to a final surface finishing process with the use of  $3 \text{ }\mu\text{m}$  diamond grit.

The aforementioned silicon carbide sintered product was immersed in an aqueous solution obtained by dissolving  $2.0 \text{ g}$  of  $\text{CaCl}_2$  in  $100 \text{ mL}$  of a  $1 \text{ weight \%}$  alumina sol aqueous solution and then placed in a drying oven and dried at  $110^\circ\text{C}$  for  $1 \text{ hour}$ . About  $0.13 \text{ mg/cm}^2$  of alumina sol in terms of  $\text{Al}_2\text{O}_3$  and about  $0.25 \text{ mg/cm}^2$  of  $\text{CaCl}_2$  in terms of  $\text{CaO}$  were found to be present in the surface of the aforementioned silicon carbide sintered product.

Next, the aforementioned silicon carbide sintered product was placed in a tubular furnace with an inside diameter of  $40 \text{ mm}$  for an oxidation treatment. The aforementioned oxidation process was carried out by passing oxygen gas into the tubular furnace at the rate of  $1 \text{ L/min}$  and maintaining the temperature at  $1,450^\circ\text{C}$  for  $3 \text{ hours}$ .

The protective film thus obtained was transparent and glass-like. The film thickness was about  $3 \text{ }\mu\text{m}$ . No defects such as pinholes, microcracks, etc., were detected. The film showed smooth surface properties.

The  $\text{Al}_2\text{O}_3/\text{SiO}_2$  molar ratio of the protective film was  $0.24$  and x-ray diffraction analysis confirmed the presence of a small quantity of cristobalite crystals.

Next, the silicon carbide sintered product with its formed protective film was placed in an Elema furnace and a piece of steel (SS41) measuring  $10 \text{ mm } \phi \times 10 \text{ mm}$  was placed on the silicon carbide sintered product as shown in Figure 1. They were heated together at  $1,200^\circ\text{C}$ ,  $1,300^\circ\text{C}$ , or  $1,400^\circ\text{C}$  for  $2 \text{ hours}$  at each temperature. When the heating temperature was  $1,200^\circ\text{C}$  or  $1,300^\circ\text{C}$ , the surface of the silicon carbide sintered

product showed no change. Upon heating at a temperature of 1,400°C, however, slight corrosion of the surface of the silicon carbide sintered product at the contact surface between the silicon carbide sintered product and the steel could be detected.

The environment of the aforementioned Elema furnace consisted of air.

#### Actual Example 2

A protective film was allowed to form on the surface of a silicon carbide sintered product as described in Actual Example 1, except that the gas used for the oxidation treatment was a gas mixture consisting of an approximately 1:1 ratio of water vapor and oxygen.

The thickness of the protective film formed was about 5  $\mu\text{m}$  and, like the protective film obtained from Actual Example 1, the film showed almost no defects and had very smooth surface properties.

Next, the reactivity with steel was tested as described in Actual Example 1. The results obtained were almost the same as those obtained in Actual Example 1, but the degree of corrosion upon heating at a temperature of 1,400°C was somewhat less than that observed in Actual Example 1.

#### Actual Example 3

A protective film was obtained as described in Actual Example 1 except that the alumina sols containing additives as shown in Table 1 were used, and, if necessary, the oxidation treatment temperature was varied.

The reactivity was tested as described in Actual Example 1, but the steel shown in

Table 1 and different heating temperatures were used to carry out the test. The amounts of each substance present in the surface of the silicon carbide sintered product in terms of their oxides, characteristics of the protective film, and the results of the test of reactivity with steel are shown in Table 1.

TABLE 1. KEY: (a) aluminum-containing substance; (b) kind; (c) amount coated in terms of oxide,  $\text{mg}/\text{cm}^2$ ; (d) other coated substances; (e) amount coated in terms of the oxide,  $\text{mg}/\text{cm}^2$ ; (f) conditions of oxidation treatment; (g) temperature,  $^{\circ}\text{C}$ ; (h) time, hr; (i) physical properties of the film; (j)  $\text{Al}_2\text{O}_3/\text{SiO}_2$  molar ratio; (k) film thickness,  $\mu\text{m}$ ; (l) results of the corrosion test; (m) type of test metal; (n) Actual Example ....; (o) Comparison Example ....; (p) alumina sol, (q) (note) results of the corrosion test, (r) O : good; (s)  $\Delta$  : somewhat good; and (t) corrosion present.

	(a) アルミニウム含有物		(d) その他塗布物		(f) 酸化処理条件		(i) 被膜物性		(l) 浸食試験結果			(m) 試験金属 の種別
	(b) 種類	(c) 酸化物換算塗布量 ( $\text{mg}/\text{cm}^2$ )	(b) 種類	(e) 酸化物換算塗布量 ( $\text{mg}/\text{cm}^2$ )	(g) 温度 ( $^{\circ}\text{C}$ )	(h) 時間 (hr)	(j) $\text{Al}_2\text{O}_3/\text{SiO}_2$ モル比	(k) 膜厚 ( $\mu\text{m}$ )	1200 $^{\circ}\text{C}$	1300 $^{\circ}\text{C}$	1400 $^{\circ}\text{C}$	
実例 1 (n)	アルミナゾル (p)	0.13	$\text{GaCl}_3$	0.23	1000	3	0.24	3	○	○	$\Delta$	SS41
2	"	"	"	"	"	"	0.13	3	○	○	$\Delta$	"
3-1	"	"	"	"	1100	10	0.49	1.3	○	○	x	"
3-2	"	"	"	"	1400	1	0.10	6	○	○	○	"
3-3	"	"	"	"	1600	1	0.30	3	○	○	$\Delta$	"
3-4	"	"	$\text{HgCl}_2$	0.36	"	3	0.24	2.3	○	○	$\Delta$	"
3-5	"	"	$\text{K}_2\text{CO}_3$	0.19	"	"	0.24	3.3	○	○	$\Delta$	"
3-6	"	"	$\text{ZnO}_2$	0.30	"	"	0.24	4.0	○	○	x	"
3-7	"	"	$\text{NaCl}$	0.13	"	"	0.24	3.0	○	○	x	"
比較例 1 (o)	-	-	-	-	-	-	-	-	○	x	x	"
2	-	-	-	-	1000	2	-	1.3	○	$\Delta$	x	"

(q) (注) 浸食試験結果 (s) (t)  
(r) ○ : 良好,  $\Delta$  : やや良, x : 浸食有

### Comparison Example 1

A silicon carbide sintered product was subjected to the surface finishing process described in Actual Example 1 and tested for its reactivity with steel using a method almost identical to the one used in Actual Example 1.

When the heating temperature was 1,200 $^{\circ}\text{C}$ , no sign of corrosion could be

detected on the surface of the silicon carbide sintered product, but when the heating temperature was higher than 1,300°C, corrosion of the surface of the silicon carbide sintered product could always be detected.

#### Comparison Experiment 2

A silicon carbide sintered product was subjected to the surface finishing process described in Actual example 1 and placed in a tubular furnace for an oxidation treatment under the same conditions used in Actual Example 1.

The oxide film that formed was white and opaque and an x-ray diffraction analysis confirmed that the film consisted mostly of cristobalite crystals.

Reactivity with steel was tested using a method almost identical to the one used in Actual Example 1.

When the heating temperature was 1,200°C, no sign of corrosion could be detected on the surface of the silicon carbide sintered product, but when the heating temperature was 1,300°C or higher, corrosion of the surface of the silicon carbide sintered product could be detected at the surface where the silicon carbide sintered product made contact with the steel, although the degree of corrosion was somewhat less than that observed in Comparison Example 1.

#### Actual Example 4

A silicon carbide sintered product was allowed to form a protective film on its surface as described in Actual Example 1 and its reactivity with steel, nickel, aluminum,

and magnesium was tested. The results obtained are shown in Table 2. The reactivity with aluminum and magnesium was tested by immersing the sample in molten aluminum or magnesium at 700°C.

TABLE 2. KEY: (a) type of metal used in the test;  
(b) results of the corrosion test and (c) Actual Example

(c)	(a) 試驗金屬の種類	(b) 浸食性試験結果			
		700℃	1200℃	1300℃	1400℃
実施例4-1	Cu	-	○	○	○
4-2	W	-	○	○	○
4-3	Al	○	-	-	-
4-4	Mg	○	-	-	-

It can be confirmed by the results shown in Table 2 that all the silicon carbide sintered products having the protective film of the present invention show excellent corrosion resistance.

As mentioned above, with the present invention, a very dense protective film with excellent mechanical strength can be formed on a silicon carbide sintered product. Silicon carbide sintered products with the aforementioned protective film can be used in a high-temperature environment in which the product makes direct contact with metals that have strong reactivity and thus can contribute greatly to the related industries.

#### 4. Brief Explanation of the Figures

Figures 1(a) and 1(b) are an oblique view and a cross-sectional diagram showing the implementation status of the corrosion tests carried out in the actual examples and comparison examples of the present invention, respectively.

(1) refractory material; (2) silicon carbide sintered product; (3) test metal; and (4) protective film layer.

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Figure 1.